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412 Rec'd PCT/PTO 19 APR 2000

PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PHASE OF
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495

To: Asst. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

(Our Deposit Account No. 03-3975

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)

Atty Dkt: PM 268729 /557778
M# /Client Ref.

From: Pillsbury Madison & Sutro LLP, IP Group: Date: April 19, 2000

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application	2. International Filing Date	3. Earliest Priority Date Claimed
<u>PCT/JP99/04455</u> <u>↑ country code</u>	19 August 1999 Day <u>MONTH</u> Year	<u>21 August 1998</u> Day <u>MONTH</u> Year (use item 2 if no earlier priority)

Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) 20 months from above item 3 date (b) 30 months from above item 3 date,
(c) Therefore, the due date (unextendable) is April 21, 2000

5. Title of Invention POLYURETHANE COMPOSITIONS

6. Inventor(s) KIMURA, et al

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

7. Please immediately start national examination procedures (35 U.S.C. 371 (f)).

8. A copy of the International Application as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

- Request;
- Abstract;
- ____ pgs. Spec. and Claims;
- ____ sheet(s) Drawing which are informal formal of size A4 11"

9. A copy of the International Application has been transmitted by the International Bureau.

10. A translation of the International Application into English (35 U.S.C. 371(c)(2))

- is transmitted herewith including: (1) Request; (2) Abstract;
(3) 20 pgs. Spec. and Claims;
(4) _____ sheet(s) Drawing which are:
 informal formal of size A4 11"
- is not required, as the application was filed in English.
- is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
- Translation verification attached (not required now).

RE: USA National Filing of PCT/JP99/04455

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11. **PLEASE AMEND** the specification before its first line by inserting as a separate paragraph:

a. --This application is the national phase of international application PCT/JP99/04455 filed August 19, 1999 which designated the U.S.--

b. --This application also claims the benefit of U.S. Provisional Application No. 60/ , filed .

12. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:

13. PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau

14. Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of **claim amendments** made before 18th month, is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).

15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))

a. is submitted herewith Original Facsimile/Copy

b. is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

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RE: USA National Filing of PCT/JP99/04455

24. Attached:

25. Preliminary Amendment:

25.5 Per Item 17.c2, cancel original pages #___, claims #___, Drawing Sheets #___26. Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:Based on amended claim(s) per above item(s) 12, 14, 17, 25, 25.5 (hilite)

Total Effective Claims	minus 20 =	x \$18/\$9 =	\$0	966/967
Independent Claims	minus 3 =	x \$78/\$39 =	\$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,		add\$260/\$130	+0	968/969

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Description

POLYURETHANE COMPOSITIONS

Technical Field

5 The present invention relates to a polyurethane composition, and more precisely, a polyurethane composition characterized in that a hindered phenol antioxidant and a specific amide compound is compounded in a polyurethane.

10 Background of the Invention

Polyurethanes are usually obtained by a polyaddition reaction of a polyisocyanate and a polyhydroxy compound, and are used in a number of fields including fibers, films, foams, leathers, paints, adhesives and the like, because of their 15 excellent physical properties with elasticity.

It has been known, however, that polyurethanes are liable to be discolored or colored, for example, caused by oxidized nitrogen gases. Particularly, when polyurethanes are produced for fiber-use, discoloring or coloring occurs in 20 routine uses such as a use in clothing. Therefore, a demand exists for a superior property of preventing discoloring or coloring.

In addition, it has been known that polyurethane is liable to be discolored or colored by heat and is yellowed 25 by thermal history during the course of production, processing and the like. Therefore, a demand also exists for a property of preventing discoloring or coloring caused by heat.

As a composition for preventing discoloring or coloring

of polyurethanes by oxidized nitrogen gases, heat or the like, a composition in which a hindered phenol antioxidant and a semicarbazide compound are compounded in polyurethane has been proposed (Japanese Patent Publication No. 2,625,508).

5 It had, however, not only a problem that a property of preventing discoloring or coloring by oxidized nitrogen gases was insufficient but also a problem that a property of preventing discoloring or coloring by heat was insufficient.

In addition, as a composition for preventing discoloring 10 or coloring of polyurethanes by oxidized nitrogen gases or the like, a composition in which an amide is compounded (JP-A-46-27874), a composition in which a hindered phenol antioxidant is compounded (JP-B-6-35538) and the like have been proposed. However, the former composition had a problem that discoloring or coloring by heat occurred, and the latter composition had a problem that a property of preventing discoloring or coloring by oxidized nitrogen gases was insufficient.

20 **Description of the Invention**

Under these circumstances, the present inventors have conducted extensive studies for finding a polyurethane composition having an excellent property of preventing discoloring or coloring not only by oxidized nitrogen gases 25 but also by heat. As the result, they have surprisingly found that a polyurethane composition having an excellent property of preventing discoloring or coloring not only by oxidized nitrogen gases but also by heat can be obtained by replacing

a specific amide with the semicarbazide compound in a composition in which a hindered phenol antioxidant and a semicarbazide compound are compounded, i.e., by compounding a hindered phenol antioxidant and a specific amide. Thus,
5 the present invention has been completed.

That is, the present invention provides a polyurethane composition, excellent in a property of preventing discoloring or coloring, characterized in that

(A) a hindered phenol antioxidant, and

10 (B) an amide represented by the following general formula

(I):



wherein R_1 represents an alkyl group having 12 to 21 carbon atoms, are compounded in a polyurethane.

15 The present invention is described below in detail.
The polyurethane used in the present invention is not particularly limited and may be one obtained by an usual process. It is obtained, for example, by polymerizing a
20 polymer having two or more terminal hydroxyl groups (polyhydroxyl polymer), particularly polyether glycol, polyester glycol or the like, with an organic diisocyanate compound to give an intermediate polymer (prepolymer) having a terminal organic isocyanate group, dissolving the obtained
25 intermediate in an inert solvent, and then adding a polyfunctional hydrogen compound to elongate chains.

The polyhydroxyl polymer herein includes, for example, polyether glycol, such as polypropylene ether glycol,

polyethylene ether glycol and polytetramethylene ether glycol, and the like.

The polyester glycol includes, for example, products obtained by polycondensing at least one of aliphatic 5 dicarboxylic acids having about 2 to 10 carbon atoms, such as succinic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid and cyclohexanedicarboxylic acid, with at least one of glycols, such as ethylene glycol, 10 propylene glycol, 1,4-butanediol, 1,6-hexanediol and neopentylene glycol. The polyester glycol includes those obtained by using an aromatic dicarboxylic acid such as 15 terephthalic acid, isophthalic acid and hydroxybenzoic acid as a co-monomer component, and lactone polyester polyols obtained by ring-opening polymerization of a cyclic ester such as 20 polycaprolactone polyester.

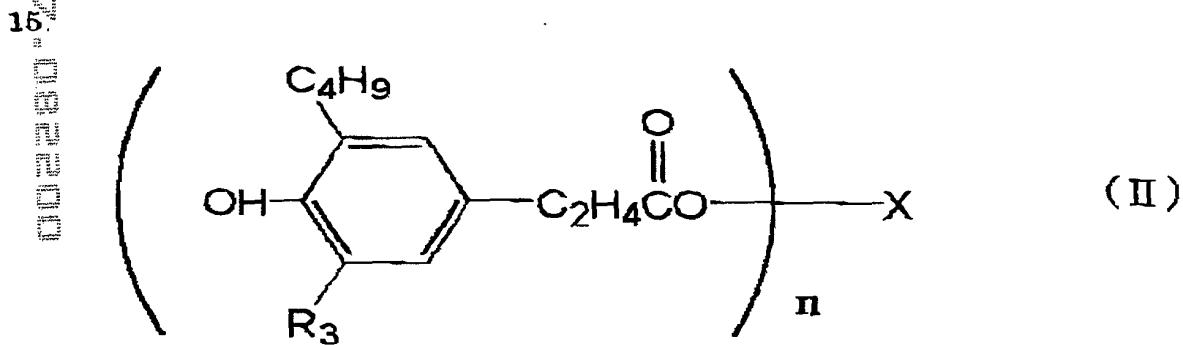
As the organic diisocyanate, there is used in the present invention, for example, at least one of 2,4-tolylene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), 25 hexamethylene diisocyanate (HDI), 1,4-phenylene diisocyanate (HDI), 1,4-phenylene diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate (HMDI), naphthalene diisocyanate, xylidine diisocyanate (XDI) and the like. Preferred diisocyanates are 25 TDI, MDI, HDI, HMDI, XDI and the like.

The polyfunctional hydrogen compound includes, for example, diamines such as ethylenediamine, propylenediamine, hexamethylenediamine, xylenediamine, 4,4'-

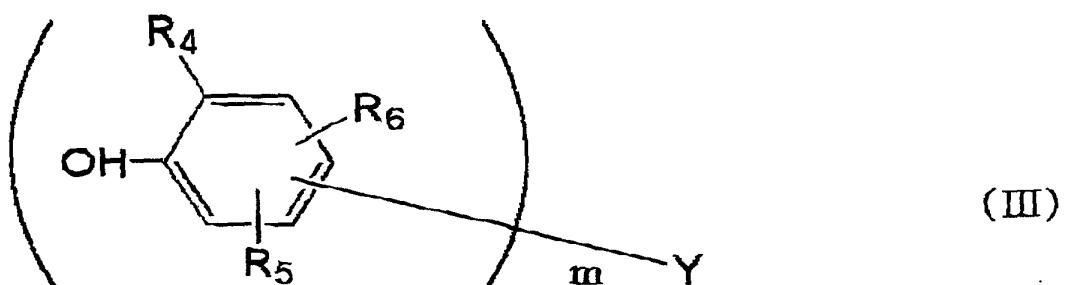
diaminodiphenylmethane and hydrazine; diols such as ethylene glycol and 1,4-butanediol; hydroxides such as water, dihydrazide, carbon dihydrazide and β -aminopropionic acid hydrazide.

5 The inert solvent used in the polymerization reaction includes polar solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N,N,N',N'-tetramethylurea, N-methylpyrrolidone, dimethylsulfoxide and the like.

The present invention is characterized in that a hindered 10 phenol antioxidant of (A) and an amide represented by the above general formula (I) are compounded. The hindered phenol antioxidant of (A) includes, for example, at least one phenol antioxidant selected from the group of compounds represented by the following general formula (II) or (III):



, wherein R₃ represents an alkyl group having 1 to 8 carbon atoms; n represents an integer of 1 to 4; and X represents an n-valent alcohol residue, having 1 to 18 carbon atoms, which 20 may optionally contain hetero atom and/or cyclic group.



wherein R₄ represents an alkyl group having 1 to 8 carbon atoms; R₅ and R₆ independently represent a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may 5 optionally contain hetero atom; m represents an integer of 1 to 3; Y represents an m-valent group, and when m is 1, it represents a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom, when m is 2, it represents a sulfur atom, an oxygen atom or an alkylidene group having 1 to 4 carbon atoms, and when m is 3, it represents an isocyanuric acid-N,N',N'''-trimethylene group or a 1,3,5-trimethylbenzene-2,4,6-trimethylene group.

R₃ in the phenol antioxidant represented by the formula (II) herein represents an alkyl group having 1 to 8 carbon atoms. Such alkyl group includes a straight chain alkyl group, a branched chain alkyl group or an alkyl group of cyclic structure, such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, tert-amyl, tert-octyl, cyclohexyl and 1-methylcyclohexyl. Preferably, it is methyl or tert-butyl. 20 It is preferred that the C₄H₉ is tert-butyl.

In addition, X represents an n-valent alcohol residue, having 1 to 18 carbon atoms, which may optionally contain hetero atom and/or cyclic group. The alcohol residue refers

to a moiety of an alcohol except its OH group. The hetero atom includes, for example, an oxygen atom, a nitrogen atom, a sulfur atom, and the like. The cyclic group includes, for example, 2,4,6,8,10-tetraoxaspiro[5.5]undecane ring.

5 benzene ring, cyclohexane ring and the like.

Representative examples of X include residues of monovalent alcohols such as methyl alcohol, ethyl alcohol, 2-ethylhexyl alcohol, octyl alcohol and octadecyl alcohol; residues of divalent alcohols such as ethylene glycol, 10 triethylene glycol, 2,2'-thiodiethanol and 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8-tetraspiro[5.5]undecane; residues of trivalent alcohols such as glycerol and N,N',N''-trihydroxyethylisocyanuric acid; residues of tetravalent alcohols such as pentaerythritol; and so on.

15 Representative examples of the phenol antioxidant represented by the formula (II) include n-octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 3,9-bis(2-(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, 20 triethylene glycol bis(3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate, tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)methane and tris[2-(3',5')-tert-butyl-4'-hydroxyhydrocinnamoyloxyethyl] isocyanurate. Amongst them, n-octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 3,9-bis(2-(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane, 25 tetrakis(methylene(3,5-di-tert-butyl-4-

hydroxyphenyl)propionate)methane, tris[2-(3',5')-tert-butyl-4'-hydroxyhydrocinnamoyloxylethyl] isocyanurate and the like are preferably used.

In addition, R₄ in the phenol antioxidant represented by the formula (III) represents an alkyl group having 1 to 8 carbon atoms. Such alkyl group includes a straight chain alkyl group, a branched chain alkyl group or an alkyl group of cyclic structure similar to those described above. Preferably, it is methyl or tert-butyl.

R₅ and R₆ independently represent a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom. The alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom, includes, for example, octylthiomethylene, 2-ethylhexylthiomethylene, N,N',-dimethylaminomethylene and the like in addition to a straight chain alkyl group, a branched chain alkyl group or an alkyl group of cyclic structure similar to those described above.

Y represents an m-valent group, and when m is 1, it represents a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom, when m is 2, it represents a sulfur atom, an oxygen atom or an alkylidene group having 1 to 4 carbon atoms, and when m is 3, it represents an isocyanuric acid-N,N',N''-trimethylene group or a 1,3,5-trimethylbenzene-2,4,6-trimethylene group. The alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom, includes, for example, groups similar to those described above. The alkylidene group

having 1 to 4 carbon atoms includes, for example, methylene, ethylidene, propylidene, butylidene and the like.

It is preferred that Y is a hydrogen atom, a methylene group, a butylidene group, a sulfur atom, a 1,3,5-5 trimethylbenzene-2,4,6-trimethylene group or the like.

Representative examples of the phenol antioxidant represented by the formula (III) include 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-4-hydroxymethylphenol, 2,2'-methylenebis(4-ethyl-6-tert-butylphenol), 2,2'-methylenebis(6-cyclohexyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylenebis(4,6-di-tert-butylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanate and 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanate. Amongst them, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanate, 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene and the like are preferably used.

Two or more hindered phenol antioxidants can be used.

The amount thereof to be compounded in the polyurethane is usually about 0.05 part by weight to 5 parts by weight.

R_1 in the amide of (B) represented by the above general formula (I) represents an alkyl group having 12 to 21 carbon atoms, which includes, for example, dodecyl, tridecyl, 5 tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl and the like.

Representative examples of preferred amide (I) include behenic acid amide, stearic acid amide and the like. Use of 10 one wherein R_1 is an alkyl having 18 to 21 carbon atoms is particularly preferred, because it is excellent in resistance against extraction by water, and therefore particularly advantageous, for example, in the field of polyurethane for fiber in which dyeing step is included.

Two or more amide (I) can be used. The amount thereof to be compounded in the polyurethane is usually 0.01 part by weight to 10 parts by weight. When the amount of the aliphatic acid amide compounded in polyurethane is less than 0.01 part by weight, the effect is liable to be insufficient; on the 20 other hand, use of an amount exceeding 10 parts by weight is not preferred from the economical viewpoint because an effect corresponding to the compounded amount is not obtained.

In addition, in the present invention, a compounding ingredient, such as ultraviolet absorbers including 25 benzotriazole, benzophenone, benzoate, cyanoacrylate, triazine or the like; stabilizers including hindered amine light stabilizer, phosphorus stabilizer, sulfur stabilizer, benzofuranone stabilizer, semicarbazide compounds or the

like; and further pigment; dye; and filler can be added, if necessary.

Specific examples of the ultraviolet absorber include the following compounds: 2-(3-tert-butyl-2-hydroxy-5-

5 methylphenyl)-5-chlorobenzotriazole, 2-(3,5-di-tert-butyl-2-hydroxyphenyl)benzotriazole, 2-(2-hydroxy-5-

methylphenyl)benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)benzotriazole, 2-(3,5-di-tert-amyl-2-

10 hydroxyphenyl)benzotriazole, 2-[2-hydroxy-3,5-bis(α,α -dimethylbenzyl)phenyl]benzotriazole, 2-hydroxy-4-

octoxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,4-

15 di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, n-hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, ethyl 2-

cyano-3,3-diphenylacrylate, 2,4-dihydroxybenzophenone,

2,2',4,4'-tetrahydroxybenzophenone, 2-(2-hydroxy-4-

octoxyphenyl)benzotriazole, 2-[2-hydroxy-3,5-bis(α,α -dimethylbenzyl)phenyl]-2H-benzotriazole, 2-(3,5-di-tert-

20 butyl-2-hydroxyphenyl)-5-chlorobenzotriazole, a condensate of methyl 3-[3-tert-butyl-5-(2H-benzotriazole-2-yl)-4-

hydroxyphenyl]propionate and polyethylene glycol (molecular weight: about 300), a hydroxyphenylbenzotriazole derivative,

2-(4,6-diphenyl-1,3,5-triazine-2-yl)-5-hexyloxyphenol and 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine-2-yl]-5-

25 octyloxyphenol.

Specific examples of the hindered amine light stabilizer include the following compounds:

bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate,
bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, 2-

methy1-2-(2,2,6,6-tetramethyl-4-piperidyl)amino-N-(2,2,6,6-tetramethyl-4-piperidyl)propionamide, bis(1,2,2,6,6-pentamethyl-4-piperidyl) 2-(3,5-di-tert-butyl-4-hydroxybenzyl)-2-n-butylmalonate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetracarboxylate, poly[{6-(1,1,3,3-tetramethylbutyl)imino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)imino}hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}], poly[{6-morpholino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)imino}hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)imino}]. a polycondensate of dimethyl succinate and 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine, a polycondensate of N,N-bis(3-aminopropyl)ethylenediamine and 2,4-bis[N-butyl-N-(1,2,2,6,6-pentamethyl-4-piperidyl)amino]-6-chloro-1,3,5-triazine, a polycondensate of 1,2,2,6,6-pentamethyl-4-piperidinol and 3,9-bis-(2-hydroxy-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane with 1,2,3,4-butanetetracarboxylic acid and bis(1-octoxy-2,2,6,6-tetramethyl-4-piperidyl) sabacate.

The benzofuranone stabilizer includes, for example

5,7-di-tert-butyl-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one and the like. The semicarbazide stabilizer includes, for example, 1,6-hexamethylenebis(N,N-dimethylsemicarbazide), 4,4'-(methylenedi-p-phenylene)bis(N,N-diethylsemicarbazide), 4,4'-(methylenedi-p-phenylene)bis(N,N-diethylsemicarbazide), 4,4'-(

(methylenedi-p-phenylene)bis(N,N-diisopropylsemicarbazide), α,α -(p-xylylene)bis(N,N-dimethylsemicarbazide), 1,4-cyclohexylenebis(N,N-dimethylsemicarbazide) and the like.

5 As to the method for compounding various stabilizers and compounding ingredients in the polyurethane, they can be compounded at any stages in the production steps. For example, they can be added directly to the polyurethane or can be added to a raw material thereof. When a solvent is used, they can
10 be added after dispersing or dissolving in a small amount of the solvent. Preferably, they are compounded after the reaction of the prepolymer with the chain-elongation agent.

According to the present invention, a polyurethane composition having an excellent property of preventing discoloring or coloring by oxidized nitrogen gases and heat can be obtained by compounding a phenol antioxidant and an amide (I) in a polyurethane. They can advantageously be used in the fields of elastic yarn, film, foam, paint, adhesive and the like. Particularly, the effect is more remarkable
20 when used as an elastic yarn.

Examples

The present invention will now be described in more detail with reference to Examples, which do not limit the scope
25 of the present invention.

[Composition]

Polyurethane	100 parts by weight
Tested stabilizer	Amount shown in Table 1

and Table 2 (parts by weight)

AO-1: 3,9-bis(2-(3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1,1-dimethylethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane,

5 AO-2: 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanate

B-1: behenic acid amide

B-2: stearic acid amide

C-1: 1,6-hexamethylenebis(N,N-dimethylsemicarbazide)

10 D-1: 2-[2'-hydroxy-3',5'-bis(α,α-dimethylbenzyl)phenyl]benzotriazole

Example 1: NO_x resistant property of preventing discoloring or coloring of polyurethane

15 Using a 30 mmΦ-single screw extruder, compositions in Table 1 described below were pelletized by melt-kneading at 185°C. The obtained pellets were exposed to 650 ppm of NO_x gas for 1 hour and the NO_x resistant property of preventing discoloring or coloring was evaluated by degree of yellowing

20 after the exposure. The results are shown in Table 1.

o: No yellowing

x: Deep yellow

25 In addition, the obtained pellets were subjected to ageing in an oven at 150°C for 3 hours. By observing the color hue after the ageing, the heat resistant property of preventing discoloring or coloring (coloring by heat) was evaluated by degree of coloring. The results are shown in Table 1.

o: Thin yellow

x: Deep yellow

Table 1

Stabilizer	Example				Comparative example				
	1	2	3	4	1	2	3	4	5
AO-1	0.5	0.5	—	—	0.5	—	—	—	0.5
AO-2	—	—	0.5	0.5	—	0.5	—	—	—
B-1	0.5	—	0.5	—	—	—	0.5	—	—
B-2	—	0.5	—	0.5	—	—	—	0.5	—
C-1	—	—	—	—	—	—	—	—	0.5
Degree of Yellowing	○	○	○	○	×	×	○	○	×
Coloring by heat	○	○	○	○	○	○	×	×	×

Example 2: Anti-leaching property of polyurethane in dyeing

Using a 30 mmΦ-single screw extruder, compositions in Table 2 described below were pelletized by melt-kneading at 165°C. Into a stainless steel vessel were placed 5 g of the obtained pellets and 100 ml of an aqueous solution at pH 5 in which 1% of Avoran IW (manufactured by Bayer), a surfactant, was added. The vessel was tightly closed and extraction was carried out at 120°C for 2 hours. The pellets before and after the extraction were exposed to 650 ppm of NO_x gas for 1 hour and a change in the NO_x resistant property of preventing discoloring or coloring by extraction was measured by evaluating degree of yellowing after the exposure. The degree of yellowing was evaluated by the following 3 scores. The results are shown in Table 2.

20 o: No yellowing; Δ: Thin yellow; x: Deep yellow

The fact that no change in the degree of yellowing was observed before and after the extraction means that it is excellent in anti-leaching property.

Table 2

Stabilizer	Example	Comparative example	
		1	2
AO-1	0.5	0.5	0.5
B-1	0.1	—	—
C-1	—	0.1	—
D-1	0.5	0.5	0.5
Degree of Yellowing			
Before extraction	○	△	×
After extraction	○	×	×

Claims

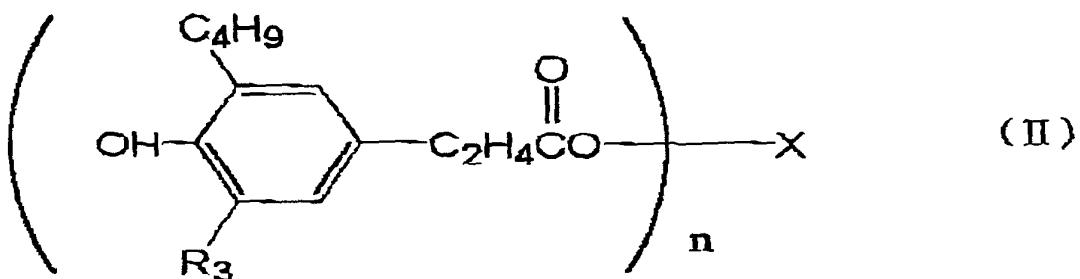
1. A polyurethane composition characterized in that
 - (A) a hindered phenol antioxidant, and
 - (B) an amide represented by the following general formula

5 (I):

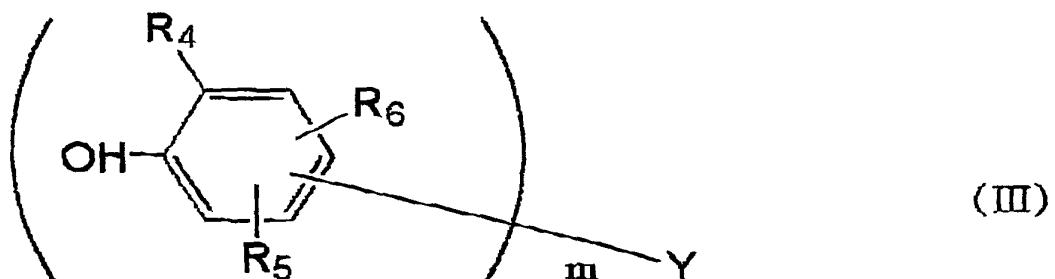


wherein R_1 represents an alkyl group having 12 to 21 carbon atoms
are compounded in a polyurethane.

10 2. The composition according to claim 1, in which the hindered phenol antioxidant is at least one selected from the group of compounds represented by the following general formula (II) or (III):



15 wherein R_3 represents an alkyl group having 1 to 8 carbon atoms; n represents an integer of 1 to 4; and X represents an n -valent alcohol residue, having 1 to 18 carbon atoms, which may optionally contain hetero atom and/or cyclic group,



wherein R₄ represents an alkyl group having 1 to 8 carbon atoms; R₅ and R₆ independently represent a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom; m represents an integer of 1 to 3; Y represents an m-valent group, and when m is 1, it represents a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom. when m is 2, it represents a sulfur atom, an oxygen atom or an alkylidene group having 1 to 4 carbon atoms, and when m is 3, it represents an isocyanuric acid-N,N',N''-trimethylene group or a 1,3,5-trimethylbenzene-2,4,6-trimethylene group.

3. The composition according to claim 1 or 2, in which the amide is at least one selected from stearic acid amide and behenic acid amide.

4. A process for preventing discoloring or coloring of polyurethane characterized in that

(A) a hindered phenol antioxidant, and

(B) an amide represented by the following general formula

20 (I):

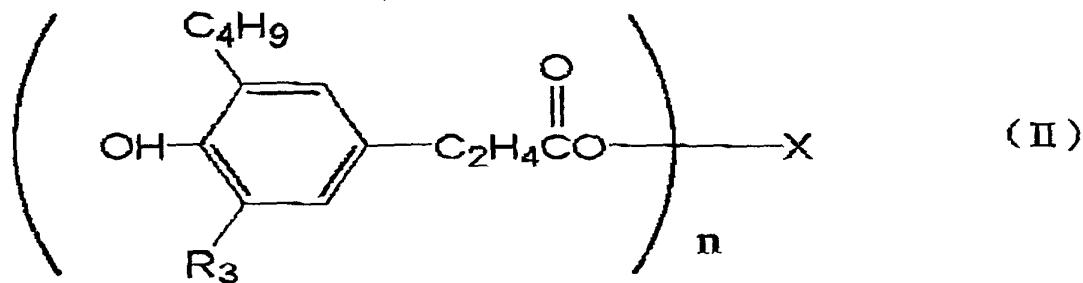


wherein R₁ represents an alkyl group having 12 to 21 carbon atoms

are compounded in the polyurethane.

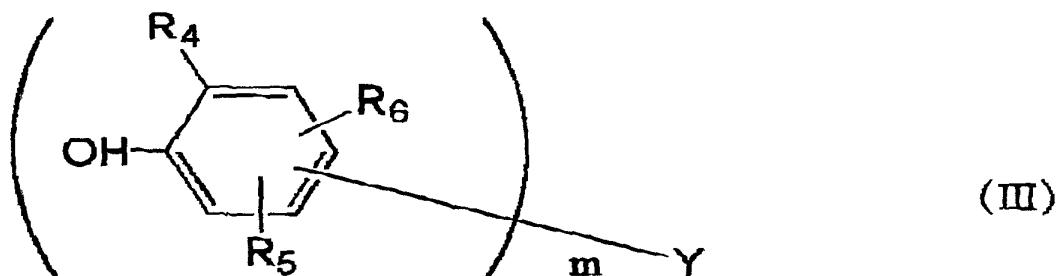
5. The process according to claim 4, in which the hindered phenol antioxidant is at least one selected from the group of compounds represented by the following general formula (II)

5 or (III):



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09529200
10-09529200

wherein R₃ represents an alkyl group having 1 to 8 carbon atoms; n represents an integer of 1 to 4; and X represents an n-valent alcohol residue, having 1 to 18 carbon atoms, which may optionally contain hetero atom and/or cyclic group.



wherein R₄ represents an alkyl group having 1 to 8 carbon atoms; R₅ and R₆ independently represent a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms, which may optionally contain hetero atom; m represents an integer of 1 to 3; Y represents an m-valent group, and when m is 1, it represents a hydrogen atom or an alkyl group, having 1 to 18 carbon atoms,

which may optionally contain hetero atom, when m is 2, it represents a sulfur atom, an oxygen atom or an alkylidene group having 1 to 4 carbon atoms, and when m is 3, it represents an isocyanuric acid- N,N',N'' -trimethylene group or a 5 1,3,5-trimethylbenzene-2,4,6-trimethylene group.

6. The process according to claim 4 or 5, in which the amide is at least one selected from stearic acid amide and behenic acid amide.

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Abstract

There is provided a polyurethane composition, which exhibits an excellent property of preventing discoloring or 5 coloring not only by oxidized nitrogen gases but also by heat, characterized in that

- (A) a hindered phenol antioxidant, and
- (B) an amide represented by the following general formula (I):



wherein R_1 represents an alkyl group having 12 to 21 carbon atoms
is compounded in the polyurethane.

DRAFTS & PROOFS

FOR UTILITY/DESIGN
CIP/PCT NATIONAL/PLANT
ORIGINAL/SUBSTITUTE/SUPPLEMENTAL
DECLARATIONS

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PM&S
FORM

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED POLYURETHANE COMPOSITIONS

the specification of which (CHECK applicable BOX(ES))
X → [] is attached hereto.

BOX(ES) → was filed on April 19, 2000 as U.S. Application No. 09/529,717
→ was filed as PCT International Application No. PCT/JP99/04455 on August 19, 1999

→ and (if U.S. or PCT application amended) was amended on

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S)		Date First Filed open or Published	Date Patented or Granted	Priority Claimed
Number	Country	Day/MONTH/Year Filed		Yes No
10-235710	Japan	21 August, 1998		X
11-124523	Japan	30 April, 1999		X

I hereby claim domestic priority benefit under 35 U.S.C. 119/120/365 of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)		Status	Priority Claimed
Application No. (series code/serial no.)	Day/MONTH/Year Filed		Yes No
		pending, abandoned, patented	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Madison & Sutro LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/organization who/which first sends/enters this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above firm and/or a below attorney in writing to the contrary.

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Edward M. Prince	22429	Paul E. White, Jr.	32011	Paul F. McQuade	31542		

1. INVENTOR'S SIGNATURE: Kenji Kimura

Date

August 10, 2000

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(FOR ADDITIONAL INVENTORS, check box [] and attach sheet (PAT-116.2) for same information for each re signature, name, date, citizenship, residence and address.)

DECLARATION AND POWER OF ATTORNEY

(continued)

ADDITIONAL INVENTORS:

Page 2

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5. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

6. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

7. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

8. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

9. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

10. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

11. INVENTOR'S SIGNATURE: _____ Date _____

Inventor's Name (typed) _____ First _____ Middle Initial _____ Family Name _____ Country of Citizenship
 Residence (City) _____ (State/Foreign Country) _____
 Post Office Address (Include Zip Code) _____

FOR ADDITIONAL INVENTORS, check box and attach sheet with same information and signature and date for each.